

We claim:

1. A method for manufacturing a microelectronic structure comprising:
  - (a) forming a first patterned resist layer comprised of holes having a first region and a second region on a substrate, said holes have a first pattern density and a first space width;
  - (b) forming a water soluble negative resist layer on said first patterned resist layer that fills the holes in the first patterned resist layer;
  - (c) patternwise exposing said water soluble negative resist layer through a mask to selectively expose portions of said water soluble negative resist layer within and adjacent to selected holes in said first patterned resist layer;
  - (d) post-expose baking said substrate to form crosslinked plugs in exposed portions of said water soluble negative resist layer, said crosslinked plugs fill selected holes in said first patterned resist layer, and to form a thin crosslinked negative resist layer in unexposed regions of said water soluble negative resist layer adjacent to the first patterned resist layer,
  - (e) removing non-crosslinked regions of said water soluble negative resist layer by applying a developer solution to form a second patterned layer comprised of the crosslinked plugs and the thin crosslinked negative resist layer wherein the second patterned layer has holes with a second space width that is smaller than said first space width and a pattern density in the first region that is different than the pattern density in the second region; and
  - (f) transferring the pattern in said second patterned layer into said substrate.

2. The method of claim 1 wherein forming said first patterned resist layer comprises the steps of patternwise exposing a positive tone resist through a mask with one or more wavelengths of radiation in a range of about 10 nm to 600 nm or with e-beam exposure and developing the exposed positive resist with a developer solution.

3. The method of claim 1 wherein the first patterned resist layer contains a residual amount of acid that diffuses into adjacent unexposed regions of the water soluble negative resist layer and catalyzes a crosslinking reaction during the post-expose baking step to form the thin crosslinked negative resist layer..

4. The method of claim 1 wherein said water soluble negative resist layer is formed from a solution comprised of a water/isopropanol solvent containing about 4 to 8 weight % of poly(vinylacetal), about 0.5 to 2 weight % of ethylene urea as a crosslinker, about 0.01 to 0.1 weight % of a photoacid generator, and about 1 to 30 ppm of a quencher.

5. The method of claim 1 wherein said water soluble negative resist is exposed with one or more wavelengths of radiation in a range of about 10 nm to 600 nm.

6. The method of claim 1 wherein said crosslinked plug has a larger width than the first space width of the holes in said first patterned resist layer.

7. The method of claim 4 wherein the amount of quencher is adjusted to produce a different thickness of the thin crosslinked negative resist layer.

8. The method of claim 1 further comprised of forming an anti-reflective coating (ARC) on the substrate prior to forming said first patterned resist layer.

9. The method of claim 2 wherein the masks used for forming the first patterned resist layer and for exposing the water soluble negative resist layer are selected from a

group including binary masks, attenuated phase shifting masks, and alternating phase shifting masks.

10. The method of claim 2 wherein the patternwise exposing step of the positive resist layer and the water soluble negative resist layer involve resolution enhancement techniques including off-axis illumination and a mask with scattering bars.

11. The method of claim 1 wherein said developer solution for removing the non-crosslinked portions of the water soluble negative resist layer comprises a water solution or an aqueous base solution.

12. The method of claim 1 wherein transferring the pattern in said second patterned layer comprises a plasma etch process.

13. The method of claim 1 wherein the holes are contact holes, vias, or trenches.

14. A method of reducing a space width and a pattern density in a resist pattern on a substrate, comprising:

(a) providing a substrate with a first patterned resist layer comprised of holes formed thereon, said substrate having a first region and a second region and said holes have a first pattern density and a first space width;

(b) forming a water soluble negative resist layer on the first patterned resist layer that fills the holes in the first patterned resist layer;

(c) patternwise exposing said water soluble negative resist layer through a mask to selectively expose portions of said water soluble negative resist layer within and adjacent to selected holes in said first patterned resist layer;

(d) post-expose baking said substrate to form crosslinked plugs in exposed portions of said water soluble negative resist layer, said crosslinked plugs fill

selected holes in said first patterned resist layer, and to form a thin crosslinked negative resist layer in unexposed regions of said water soluble negative resist layer adjacent to the first patterned resist layer, and

(e) removing non-crosslinked regions of said water soluble negative resist layer by applying a developer solution to form a second patterned layer comprised of the crosslinked plugs and the thin crosslinked negative resist layer wherein the second patterned layer has holes with a second space width that is smaller than said first space width and a pattern density in the first region that is different than the pattern density in the second region.

15. The method of claim **14** wherein forming said first patterned resist layer comprises the steps of patternwise exposing a positive tone resist through a mask with one or more wavelengths of radiation in a range of about 10 nm to 600 nm or with e-beam exposure and developing the exposed positive resist with a developer solution.

16. The method of claim **14** wherein the first patterned resist layer contains a residual amount of acid that diffuses into adjacent unexposed regions of the water soluble negative resist layer and catalyzes a crosslinking reaction during the post-expose baking step to form the thin crosslinked negative resist layer.

17. The method of claim **14** wherein said negative resist layer is formed from a solution comprised of a water/isopropanol solvent containing about 4 to 8% of poly(vinylacetal), about 0.5 to 2% of ethylene urea as a crosslinker, about 0.01 to 0.1% of a photoacid generator, and about 1 to 30 ppm of a quencher.

18. The method of claim **14** wherein said negative resist is exposed with one or more wavelengths of radiation in a range of about 10 nm to 600 nm.

19. The method of claim **14** wherein said crosslinked plug has a larger width than the first width of the holes in said first patterned resist layer.

20. The method of claim **17** wherein the amount of quencher is adjusted to produce a different thickness of the thin crosslinked negative resist layer.

21. The method of claim **14** wherein an anti-reflective coating (ARC) is formed on the substrate prior to forming said first patterned resist layer.

22. The method of claim **21** wherein an ARC has a refractive index (n and k values) that is selected to optimize the process of forming a first patterned resist layer on said substrate.

23. The method of claim **15** wherein the masks used for forming the first patterned resist layer and for exposing the water soluble negative resist layer are selected from a group including binary masks, attenuated phase shifting masks, and alternating phase shifting masks.

24. The method of claim **15** wherein the patternwise exposing step of the positive resist layer and the water soluble negative resist layer involve resolution enhancement techniques including off-axis illumination and a mask with scattering bars.

25. The method of claim **14** wherein said first patterned layer is further comprised of a third region having holes with a first space width and a pattern density unequal to the first pattern density and wherein the second patterned layer reduces the first space width to a second space width in the third region but does not change the pattern density in the third region.

26. The method of claim **14** wherein said substrate is comprised of a plurality of regions and the first patterned layer has a plurality of holes in each region.

27. The method of claim **14** wherein the first patterned layer in the first and second regions of the substrate is comprised of dense holes and the second patterned layer is comprised of an isolated hole in the first region and dense holes in the second region.

28. A method of reducing a space width and a pattern density in a resist pattern, comprising:

(a) providing a substrate with a first patterned resist layer comprised of holes formed on an ARC layer, said substrate having a first region and a second region and said holes have a first pattern density and a first space width;

(b) forming a water soluble negative resist layer comprised of a polar polymer on the first patterned resist layer;

(c) patternwise exposing said water soluble negative resist layer through a mask to selectively expose portions of said water soluble negative resist layer within and adjacent to selected holes in said first patterned resist layer;

(d) post-expose baking said substrate to form water insoluble plugs in exposed portions of said water soluble negative resist layer, said water insoluble plugs fill selected holes in said first patterned resist layer, and to form a thin water insoluble negative resist layer in unexposed regions of said water soluble negative resist layer adjacent to the first patterned resist layer, and

(e) removing the remaining water soluble portions of said water soluble negative resist layer by applying a developer solution to form a second patterned layer comprised of the water insoluble plugs and the thin water insoluble negative resist layer wherein the second patterned layer has holes with a second space width that

is smaller than said first space width and a pattern density in the first region that is different than the pattern density in the second region.

29. The method of claim **28** wherein forming said first patterned resist layer comprises the steps of patternwise exposing a positive tone resist through a mask with one or more wavelengths of radiation in a range of about 10 nm to 600 nm or with e-beam exposure and developing the exposed positive resist with a developer solution.

30. The method of claim **28** wherein the first patterned resist layer contains a residual amount of acid that diffuses into adjacent unexposed regions of the water soluble negative resist layer during the post-bake step and catalyzes a reaction that converts a water soluble polymer to a non-polar polymer that is insoluble in water to form the thin water insoluble negative resist layer.

31. The method of claim **28** wherein said water soluble negative resist layer contains a quencher to control acid diffusion during the post expose bake step.

32. The method of claim **28** wherein said water soluble negative resist is exposed with one or more wavelengths of radiation in a range of about 10 nm to 600 nm.

33. The method of claim **28** wherein said water insoluble plug has a larger width than the first width of the holes in said first patterned resist layer.

34. The method of claim **31** wherein the amount of quencher is adjusted to produce a different thickness of the thin water insoluble negative resist layer.

35. The method of claim **28** further comprised of etching through the ARC layer at the bottom of the holes formed in the second patterned layer and performing a plasma etch to transfer the pattern in the second patterned layer into said substrate.

36. The method of claim **29** wherein the masks used for forming the first patterned resist layer and for exposing the water soluble negative resist layer are selected from a group including binary masks, attenuated phase shifting masks, and alternating phase shifting masks.

37. The method of claim **29** wherein the patternwise exposing step of the positive resist layer and the water soluble negative resist layer involve resolution enhancement techniques including off-axis illumination and a mask with scattering bars.

38. The method of claim **28** wherein said substrate is comprised of a plurality of regions and the first patterned layer has a plurality of holes with a first space width in each region and wherein the holes in said second patterned layer have a second space width in the plurality of regions.

39. The method of claim **28** wherein the first patterned layer in the first and second regions of the substrate is comprised of dense holes and the second patterned layer is comprised of an isolated hole in the first region and dense holes in the second region.

40. A water soluble negative resist composition, said composition comprising:

- (a) a polymer containing vinylacetal groups;
- (b) an ethyleneurea crosslinker;
- (c) a photoacid generator; and
- (d) a quencher.

41. The water soluble negative resist composition of claim **40** wherein the photoacid generator is selected from the group consisting of onium salts, imidosulfonates, and diazoketone sulfonates.



42. The water soluble negative resist composition of claim **40** wherein the solvent is further comprised of isopropanol.

43. The water soluble negative resist composition of claim **40** wherein the quencher is selected from a group consisting of amines, nitrogen containing compounds and derivatives thereof.

44. The composition of claim **40** wherein the composition is comprised of about 90 to 95 parts of a water/isopropanol mixture, about 4 to 8 parts poly(vinylacetal), about 0.5 to 2 parts ethyleneurea, about 0.01 to 0.1 parts photoacid generator, and about 1 to 30 ppm of a quencher.

45. The water soluble negative resist composition of claim **40** which is spin coated to form a negative resist layer on a substrate that is patterned by a process comprising exposure with one or more wavelengths of radiation in a range of about 10 nm to 600 nm or with electron beam exposure.

46. The water soluble negative resist composition of claim **45** that does not mix with an underlying patterned resist layer comprised of a positive tone composition.